



Production of hexane from sorbitol in aqueous medium over Pt/NbOPO₄ catalyst



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ARTICLE INFO

Article history:

Received 24 April 2015

Received in revised form 24 August 2015

Accepted 30 August 2015

Available online 1 September 2015

Keywords:

Sorbitol

Hexane

Dehydration

Hydrogenolysis

ABSTRACT

Liquid bio-fuels derived from renewable biomass are of great importance on the potential substitution for the diminishing fossil fuels. Aqueous-phase process of sugar and sugar-derived molecules can be used to produce a range of alkanes and oxygenates. In this work, Pt/NbOPO₄ multifunctional catalyst was used in the alkane production by the hydrodeoxygenation of sorbitol in aqueous solution. The results indicated that Pt/NbOPO₄ catalyst showed the highest activity with 60% yield of C₆ and C₅ alkanes at 250 °C and 4 MPa H₂ among a series of catalysts. The reaction pathway showed that this process included dehydration, hydrogenolysis and CC bond cleavage. Isosorbide is the product of dehydration reaction and also an important intermediate in this process, which undergoes ring opening and following hydrogenolysis to form C₆ hexane. The activation energy of sorbitol dehydration and isosorbide hydrogenolysis was calculated, that is 72.7 kJ/mol and 147.6 kJ/mol, respectively, over Pt/NbOPO₄ catalyst, much lower than those over Pt/ZrP and Pt/H-Beta catalysts, which would be attributed to the strong and high acid amount of NbOPO₄ as well as the promotion effect of NbO_x for CO bond cleavage. The above results also showed that isosorbide hydrogenolysis is the rate-determine step. More importantly, Pt/NbOPO₄ catalyst was very stable, there was nearly no decrease of sorbitol conversion and no change of products distribution after working in a fixed bed reactor for 100 h. Therefore, Pt/NbOPO₄ is an efficient and stable catalyst for hexane production from sorbitol in aqueous media.

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1. Introduction

Nowadays, with the diminishing of fossil fuel resources and the growing of environmental concerns (such as CO₂ and SO₂ emissions from the utilization of fossil energy), the replacement of petrochemical-based routes for the production of liquid fuels by renewable biomass is receiving more and more attention [1]. In this respect, Lignocellulose is the only current renewable source of organic carbon that can be converted to liquid fuels due to low cost, not competing with food supply and wide spread [2,3]. Most studies for liquid fuel production using biomass as feedstock was currently limited to bio-oils [4–6] produced by pyrolysis or liquefaction of biomass platform compounds, such as HMF [7–10], furfural [11,12], levulinic acid [13,14], monofunctional hydrocarbons [15] or sugar alcohols [16–20]. Notably, a novel process called as aqueous phase

process for the production of alkanes (C₅ and C₆) from sugar polyols such as sorbitol was initially proposed by Dumesic in 2004 [21]. Since the alkane products spontaneously separated from the liquid phase in this process without energy-intensive distillation and purification steps, thus, the overall thermal efficiency of the process can be greatly improved [22]. Based on the above technology, renewable gasoline could be obtained from lignocellulosic biomass in such a reaction route that lignocelluloses were firstly converted to sugars, then polyols, and finally heavier alkanes (C₅, C₆), which can be added directly to fossil gasoline for transportation applications [23].

As a result, increasing attention has been attracted on this process. For instance, Li and Huber identified the reaction intermediates and reaction chemistry for the aqueous-phase hydrodeoxygenation of sorbitol over a bifunctional catalyst (Pt/SiO₂–Al₂O₃) that contains both metal and acid sites [23]. They also reported the aqueous-phase hydrodeoxygenation of sorbitol over two fundamentally different types of bifunctional catalysts: Pt/ZrP and Pt–ReO_x/C in a continuous flow reactor [24,25]. The gasoline-range yield of each catalyst was 66.8% and 44.4% for the

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Pt/ZrP and Pt-ReO_x/C catalysts, respectively, but Pt-ReO_x/C has a higher hydrothermal stability than that of Pt/ZrP. Afterwards, Dumesic et al. reported the aqueous-phase dehydration and hydrogenation of sorbitol to alkanes with commercial niobium supported Pt as catalyst at temperatures near 257 °C and pressures of 5.4 MPa, 50% yield of alkanes (C1–C6) was obtained [26]. The author considered that this high reactivity is not related to the concentration of acid sites but rather is attributed to the coordination environment of the niobium acid center. Zhang et al. also reported the utilization of solid acid supported non-noble metal catalyst (Ni/HZSM-5) in sorbitol transformation, 36.5% yield of C5 and C6 were obtained [27]. By adjusting the activity of catalyst with MCM-41, the yield of C5 and C6 could be improved to 60%, but the stability of catalyst is a big challenge in a practical application [28]. Recently, Chen et al. [29] reported high yields of *n*-hexane and *n*-pentane by hydrogenolysis of aqueous sorbitol and xylitol, respectively, at 413–443 K by using the Ir-ReO_x/SiO₂ catalyst combined with H-ZSM-5 as a co-catalyst. This is an interesting work, but is involved the use of high-cost solvent (*n*-dodecane).

Among liquid alkanes, *n*-hexane is not only used as fuel but also as nonpolar solvent because of their colorless and chemical inertia [30]. Aqueous phase process provides an efficient route for the production of liquid alkanes from biomass-derived sorbitol, while the main reaction of hexane formation always combined with sorbitol reforming into H₂ and CO₂, which has been identified by Dumesic and co-workers over a bifunctional metal-acid catalyst [21,23]. In most cases, the selectivity to hexane is very low because of the severe CC cracking reactions. Therefore, catalysts that cleave more C–O bond but do not promote the cleavage of CC chain will be desired for sorbitol conversion to alkane in the future, not only in the field of fuel production but also for chemical production. It was reported that supported Pt and Pd catalysts with mineral acids were effective in C–O bond cleavage [31,32]. It has also been suggested that the reaction rate for C–O bond cleavage is proportional to the Brönsted acid site concentration on the solid acid catalyst [26,33]. Our previous work showed that mesoporous niobium phosphate supported Pd catalyst was an excellent catalyst on production of liquid alkanes from furan-based compounds and NbO_x species played the key role in C–O cleavage [34].

Herein, a mesoporous niobium phosphate supported Pt multifunctional catalyst was developed for sorbitol transformation into alkanes in aqueous media. In this process, the reactions mainly included dehydration, C—O cleavage and less CC cleavage was desired for the production of C6 alkane because the CC bond cleavage would lead to the formation of methane, ethane and even CO/CO₂. Very recently, we found that Pd/NbOPO₄ catalyst was an excellent catalyst for the production of alkanes from furan-based compounds in an inert solvent and NbO_x played very important role in C–O bond cleavage [34]. Here, Pt/NbOPO₄ catalyst gave the best yield of C6 and C5 alkanes among a series of Pt-based and NbOPO₄-based catalysts during the hydrodeoxygenation of sorbitol in aqueous medium. Furthermore, we also figured out the reaction route of this process combined with the kinetic experiments and investigated a series of reaction parameters of this process. Finally, the stability of Pt/NbOPO₄ catalyst was also studied.

2. Experimental

2.1. Materials

Sorbitol was purchased from Shanghai Linfeng Chemical Reagent Co., Ltd. H-Beta zeolite and ZSM-5 were both purchased from Nankai University Catalyst Co., Ltd. γ -Al₂O₃ was provided by BASF chemical company. RuCl₃·3H₂O (37%), Pd(NO₃)₂ and Rh(NO₃)₃ were all purchased from Aladdin Reagent Limited Com-

pany. Hexane and Pentane were purchased by Shanghai Chemicals Company. All other chemicals were of analytic grade which was used directly without further purification.

2.2. Preparation of catalysts

Nb precursor (Nb-tartrate) and mesoporous NbOPO₄ were prepared according to the literatures [35,36]. The details for the preparation of mesoporous NbOPO₄ was as follows: 1.32 g (0.01 mol) of diammonium hydrogen phosphate was dissolved in 20 ml water and the initial pH was adjusted to 2 by using phosphoric acid. With continuous stirring, 20 ml of 0.5 M niobium tartrate (pH 2) was added to the above solution. Then the mixed solution was dropped into the aqueous solution of cetyltrimethyl ammonium bromide (CTAB) which was previously prepared by dissolving 1.0 g of CTAB in 13 ml of distilled water. Furthermore, the mixture was stirred for additional 60 min at 35 °C, and then the transparent solution was aged in a Teflon-lined autoclave for 24 h at 160 °C. After aging, it was cooled down and the obtained solid was filtered, washed with distilled water and then dried at 50 °C. Finally, NbOPO₄ sample was obtained by calcination at 500 °C for 5 h in air to remove template.

The synthesis of mesoporous Nb₂O₅ is similar to mesoporous NbOPO₄ except the addition of phosphate precursor. Typically, 1.0 g of CTAB (cetyltrimethyl ammonium bromide) was dissolved in 15 ml of ethanol (or H₂O) at 35 °C. Then 40 ml of 0.25 M niobium tartrate was dropped into the above solution with continuous stirring. After stirred at 35 °C for 1 h, the mixture was aged in a Teflon-lined autoclave for 24 h at 160 °C. The aged mixture was then filtered, washed with distilled water and ethanol, respectively before drying at 50 °C overnight, following by calcination in air at 500 °C for 5 h with a linear heating ramp of 1 °C min^{−1}.

The Pt/NbOPO₄ catalyst was prepared by incipient wetness impregnation method. Firstly, the water adsorption of NbOPO₄ was measured. Based on that, the Pt/NbOPO₄ catalyst was prepared by impregnating the supports with calculated amount aqueous solution of Pt(NO₃)₂·xH₂O as Pt precursor. After impregnation, the catalysts were dried at 100 °C for 12 h, followed by calcination in air at 500 °C for 3 h with a linear heating ramp of 1 °C min^{−1}. As references, H-ZSM-5, γ -Al₂O₃ and H-Beta supported Pt catalysts were also prepared by the method similar to the case of Pt/NbOPO₄. Besides Pt, other M (M = Pd, Rh, Ir, Rh and Ni) loaded NbOPO₄ catalysts were also prepared using above method.

2.3. Characterization of catalysts

Transmission electron microscopy (TEM) images were recorded on a FEI Tecnai F20 s-TWIN instrument, and the electron beam accelerating voltage was 200 kV. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the apparent surface areas. Thermal gravimetric (TG) analysis was performed at a heating rate of 10 K min^{−1} from 40 to 800 °C in flowing air using a WCT-2 thermal analyzer (PerkinElmer Diamond TG-DTA). Temperature-programmed desorption of ammonia (NH₃-TPD) was carried out in an apparatus (PX200, Tianjin Golden Eagle Technology Co., Ltd.) equipped with a thermal conductivity detector (TCD). The samples (100 mg) were loaded into a U-shaped quartz tube. Prior to TPD measurements, the samples were pretreated in flowing N₂ (45 ml min^{−1}) for 1 h at 500 °C, and then cooled to 50 °C. NH₃ was adsorbed onto the samples by exposure to flowing 10% NH₃ in N₂ gas mixture (50 ml min^{−1}) for 45 min at 50 °C. Residual and physical adsorbed NH₃ was removed by purging the samples with flowing N₂ (45 ml min^{−1}) at 90 °C for 1 h. Desorption of NH₃ was performed by heating the samples at a rate of 10 °C min^{−1} under flowing N₂ (45 ml min^{−1}) from 90 °C to 800 °C.

Table 1
Hydrogenolysis of sorbitol over NbOPO₄ supported bifunctional catalysts.^a

Entry	Catalyst	T/°C	Reaction time/h	Sorbitol conversion/%	Yield/%		
					Hexane	Pentane	Isosorbide
1	4wt%Pt/NbOPO ₄	250	12	>99	55.9	4.8	5.3
2	4wt%Pd/NbOPO ₄	250	12	>99	23.5	5.1	9.1
3	4wt%Ru/NbOPO ₄	250	12	>99	8.9	7.8	36.7
4	4wt%Ir/NbOPO ₄	250	12	>99	6.1	3.1	48.9
5	4wt%Rh/NbOPO ₄	250	12	>99	10.2	15.2	23.1
6	10wt%Ni/NbOPO ₄	250	12	90	0.9	0.4	60.2

^a Reaction condition: sorbitol (1 g), H₂O (20 g), catalysts (0.3 g), 4 MPa H₂, 250 °C, 12 h; other oxygenated products are sorbitan, 2-(tetrahydrofuran-2-yl)ethan-1-ol and hexanol.

2.4. Procedure for sorbitol conversion and product analysis

The catalytic activity test was carried out in a batch-type high-pressure autoclave reactor with a capacity of 100 ml. Typically, 1 g of sorbitol and 0.3 g of the catalyst were filled in the reactor with 20 ml of deionized water per run. Prior to activity test, H₂ was displaced for three times so as to remove oxygen contained in the reactor, and then the reaction was performed at the desirable reaction temperature and hydrogen pressure, the stirring speed is about 600 r/min. After reaction, the organic phase was extracted by cyclohexane and then analyzed by GC equipped with flame ionization detector (FID). The yields of liquid alkanes (mainly hexane and pentane) were determined using internal standard method by adding dodecane as internal standard after reaction. The aqueous phase was analyzed by HPLC (Agilent, 1200 series) equipped with a Shodex SUGAR SC1011 column (8 × 300 mm) with a refractive index detector (Agilent G1362A) by using high pure water as a mobile phase at a flow rate of 0.8 ml/min at 50 °C. The gas phase was collected in a gas bag carefully and analyzed by GC equipped with a packed column, a methanizer (for CO₂ or CO detection) and a flame ionization detector.

$$Y(\text{hexane or pentane})\% = \frac{\text{moles of hexane or pentane by GC}}{\text{(moles of sorbitol)}} \times 100\%$$

The direct hydrodeoxygenation of sorbitol was also tested in a fixed-bed reactor system. A feed composed of a 10 wt% aqueous solution of sorbitol and a co-feed of H₂ was used for the flow reaction test. 2.0 g of 40–60 mesh pelletized catalyst was loaded into the stainless steel tubular reactor (inner diameter of 6 mm, length of 55 cm). The crushed quartz granules were placed into the both ends of the catalyst to maintain bed height and reduce the dead volume. After the loading, the reaction temperature and pressure were adjusted to the desired value and the feed flow was injected by an HPLC pump with 40 ml min⁻¹ flowing H₂. The weight hourly space velocity (WHSV) was determined through dividing the mass flow rate of the liquid by the mass of the catalyst used. The liquid phase was separated from gas phase and collected by a gas-liquid separator. The gas phase was analyzed by GC equipped with a packed column, a methanizer and a flame ionization detector. Liquid phase analysis was performed with an Agilent 7890 GC–MS equipped with

a HP-5 column. Liquid and gas phases were sampled and analyzed every 2 h.

3. Results and discussion

3.1. Sorbitol conversion in batch reactor

Firstly, a series of NbOPO₄-supported multifunctional catalysts were prepared for hydrogenolysis of sorbitol into alkanes. As shown in Table 1, Pt/NbOPO₄ showed the best performance with a total yield of hexane and pentane over 60% and an hexane yield over 55% (Table 1, entry 1), the remaining products were mainly isosorbide, 1-hexanol, 1-pentanol, C₁–C₄ alkanes and other oxygenated compound. However, other NbOPO₄ supported catalysts showed poor performance for the production of hexane and pentane, the activity decreased in the following order: Pt > Pd > Rh > Ru > Ir > Ni (Table 1, entries 2–6). The total yield of hexane and pentane was only 28.9% in the case of Pd/NbOPO₄ catalyst, less than half of Pt/NbOPO₄ catalyst, which was attributed to increasing of oxygenated compounds, especially isosorbide according to Table 1. For Ni/NbOPO₄ catalyst, almost no hexane and pentane were detected, the main product was isosorbide. So isosorbide might be an important intermediate in the whole process, which would be discussed later.

In order to further investigate the effect of support on hydrogenolysis of sorbitol, a series of Pt-based bifunctional catalysts were prepared and applied in the above reaction. The catalytic performance is collected in Table 2. When using Pt-loading H-ZSM-5, H-Beta, Nb₂O₅ and Al₂O₃ as catalysts, the total yield of hexane and pentane dropped dramatically (Table 2, entries 2–5). However, the content of oxygenated compounds increased largely and isosorbide was still the main product. The Pt/H-Beta catalyst showed relatively better performance among these catalysts, but only 37.5% yield of hexane and pentane was obtained, the lowest yield of hexane and pentane was obtained over Pt/Al₂O₃ catalyst due to low acidity. The Pt/Nb₂O₅ catalyst, which contained similar acidity with Pt/Al₂O₃ catalyst and possessed a large amount of NbO_x species, also showed bad performance, but the yield of hexane and pentane is higher than that of Pt/Al₂O₃ catalyst (Table 2, entries 4). The above results indicated that the promotion effect of NbO_x species

Table 2
Hydrogenolysis of sorbitol over 4wt% Pt-based catalysts.^a

Entry	Catalyst	Pt content by ICP/%	Total acid amount ^b (Area)	Sorbitol conversion/%	Yield/%		
					Hexane	Pentane	Isosorbide
1	Pt/NbOPO ₄	3.9	4914.7	>99	55.9	4.8	5.3
2	Pt/H-Beta	3.8	2159.8	>99	32.6	4.9	12.9
3	Pt/HZSM-5	3.9	3084.7	97.3	27.5	6.2	13.9
4	Pt/Nb ₂ O ₅	3.8	1237.3	95.9	13.1	3.4	14.2
5	Pt/Al ₂ O ₃	3.7	1432.6	96.2	3.2	1.5	16.8

^a Reaction condition: sorbitol (1 g), H₂O (20 g), catalysts (0.3 g), 4 MPa H₂, 250 °C, 12 h; other oxygenated products are sorbitan, 2-(tetrahydrofuran-2-yl) ethan-1-ol and hexanol.

^b Total acid amount of catalyst support determined by NH₃-TPD, that of all catalysts was conducted with the same catalyst amount(0.1 g).

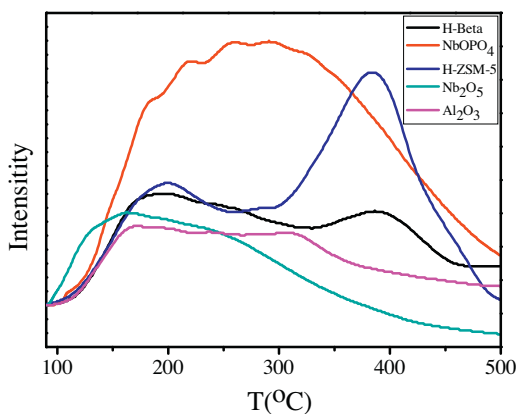


Fig. 1. The NH_3 -TPD measurements of a series of solid acids.

was not the only factor for C–O bond cleavage, and the other properties of the catalysts such as hydrogenation property of the metal (Table 1) and acid properties of the supports (Fig. 1) are also of significant importance. The catalyst with high acidity was more favorable for the production of C6, which was mainly beneficial to the dehydration of sorbitol.

3.2. Influence of reaction conditions

The hydrogenolysis of sorbitol in aqueous medium into hexane was also depended on reaction parameters, e.g. reaction temperature, reaction time and hydrogen pressure (Fig. 2). The effects of reaction temperature on the activity and product yield in sorbitol hydrogenolysis into hexane were examined over Pt/NbOPO_4 catalyst under the condition of 4 MPa H_2 and 10 h. It can be seen that with the increase of reaction temperature, the conversion of sorbitol changed slightly. However, below 250 °C, the yield of hexane increased successively with the increase of temperature. With the further increase of reaction temperature, the hexane yield decreased slightly. A small number of pentane was produced due to CC bond cleavage during hydrogenolysis. We could also observed from Fig. 2(A) that oxygenated compounds, including isosorbide, sorbitan, 1-hexanol, 1-pentanol, and other minor oxygenated compound, was the main product at low temperature and then decreased successively with temperature increasing. Therefore, 250 °C was selected as the optimal reaction temperature. Similarly, the influence of hydrogen pressure in the range of 1–5 MPa was investigated at 250 °C and shown in Fig. 2 (B). It can be seen that the yield of hexane was improved with pressure increased till 4 MPa H_2 . Further increasing H_2 pressure has no influence on the hexane yield. Oxygenated compounds were also the main product at low hydrogen pressure and then decreased successively with hydrogen pressure increasing. Therefore, 4 MPa was selected as the optimal hydrogen pressure. The effect of Pt loading amount on the performance of aqueous-phase process of sorbitol was also investigated in Fig. 2 (D). The sorbitol conversion changed slightly but the hexane yield increased from 18.9% to 57.1% as Pt loading amount from 2% to 4% over NbOPO_4 support, and then decreased slightly as Pt loading amount further increased to 5%, which probably resulted from more CC bond cleavage. Therefore, 4% Pt over NbOPO_4 was the optimal loading amount.

3.3. Investigation of reaction pathways

In order to investigate the reaction pathway of the hydrogenolysis of sorbitol into C6, the reaction was monitored as a function of time. According to Fig. 2(C), the main products included sorbitan, isosorbide, 2-(tetrahydrofuran-2-yl) ethan-1-ol, hexanol, hexane

Table 3

The activation energy data of Pt-based catalysts.

Catalysts	Activation energy/kJ/mol	
	Ea1	Ea2
Pt/ NbOPO_4	72.7	147.6
Pt/H-Beta	92	171.3

and pentane in the liquid phase, the yield of all kinds of products in the liquid phase was also presented in Fig. 2(C). After reaction for 1 h, a trace amount of sorbitan, isosorbide, hexanol and hexane was existed, along with large amount of unreacted sorbitol. When the reaction was extended to 4 h, the amount of hexane, isosorbide and hexanol increased continually and the isosorbide yield reached maximum. After another 2 h reaction, the hexane yield continued to increase, while the yield of isosorbide reduced and the yield of hexanol reached maximum. When the reaction was further extended to 12 h, hexane was found as the only major product, along with small amounts of CC cleavage products (C5), and small amounts of intermediates left in the liquid phase. According to above results, we could know that isosorbide and hexanol are two major oxygen-containing intermediates during the production of hexane from sorbitol. Therefore the main pathway of sorbitol hydrogenolysis into hexane was put forward in our system as below (Scheme 1). The sorbitol was firstly dehydrated into isosorbide and then converted into hexane by continuous hydrogenolysis.

3.4. Kinetic study

In order to further elucidate this process, the whole reaction was divided into two steps, namely the dehydration of sorbitol and hydrogenolysis of isosorbide, and then we systematically investigated which step is a rate-determining step by kinetic study. First, we performed kinetic analysis of the dehydration of sorbitol with Pt/NbOPO_4 as catalyst. According to previous report [37], the sorbitol dehydration reaction was a first-order dependence on the reactant concentration. If the sorbitol dehydration reaction is considered to follow the first-order kinetics, a plot of $\ln C_{\text{sorbitol}}$ as a function of time will be linear, with a slope equal to negative value of the reaction rate constant k , as proposed by Kuster [38]. Fig. 3a shows that the plots of $\ln C_{\text{sorbitol}}$ vs. reaction time at different reaction temperatures (ranging from 200 to 240 °C) over Pt/NbOPO_4 catalyst and obtained straight lines, validating the first-order reaction model. The slopes of the lines provided the rate constants (k) at different temperatures and were used to determine the activation energy (Ea1) using Arrhenius equation. The activation energy was 72.7 kJ/mol as shown in Fig. 3b, with the corresponding pre-exponential factor of $6.2 \times 10^5 \text{ min}^{-1}$. Similarly, the kinetic analysis of isosorbide hydrogenolysis with Pt/NbOPO_4 as catalyst was also investigated. A plot of $\ln C_{\text{isosorbide}}$ as a function of time also presented linear model according to Fig. 4a. Therefore the isosorbide hydrogenolysis was also considered to follow the first-order kinetics. Fig. 4a shows that the plots of $\ln C_{\text{isosorbide}}$ vs. reaction time at different reaction temperatures (ranging from 230 to 250 °C) over Pt/NbOPO_4 catalyst. The activation energy (Ea2) was 147.6 kJ/mol as shown in Fig. 4b, with the corresponding pre-exponential factor of $2.2 \times 10^{12} \text{ min}^{-1}$. Therefore we could know that the activation energy of sorbitol dehydration and isosorbide hydrogenolysis are 72.7 kJ/mol and 147.6 kJ/mol respectively, which indicated that the sorbitol dehydration proceeded more easily than isosorbide hydrogenolysis did in our system and isosorbide hydrogenolysis into hexane was an energy-intensive process. Therefore the process of isosorbide hydrogenolysis was a rate-determining step during the whole process for hexane production from sorbitol.

In order to show the superiority of Pt/NbOPO_4 in this reaction, we also performed kinetic analysis of $\text{Pt}/\text{H-Beta}$ catalyst for com-

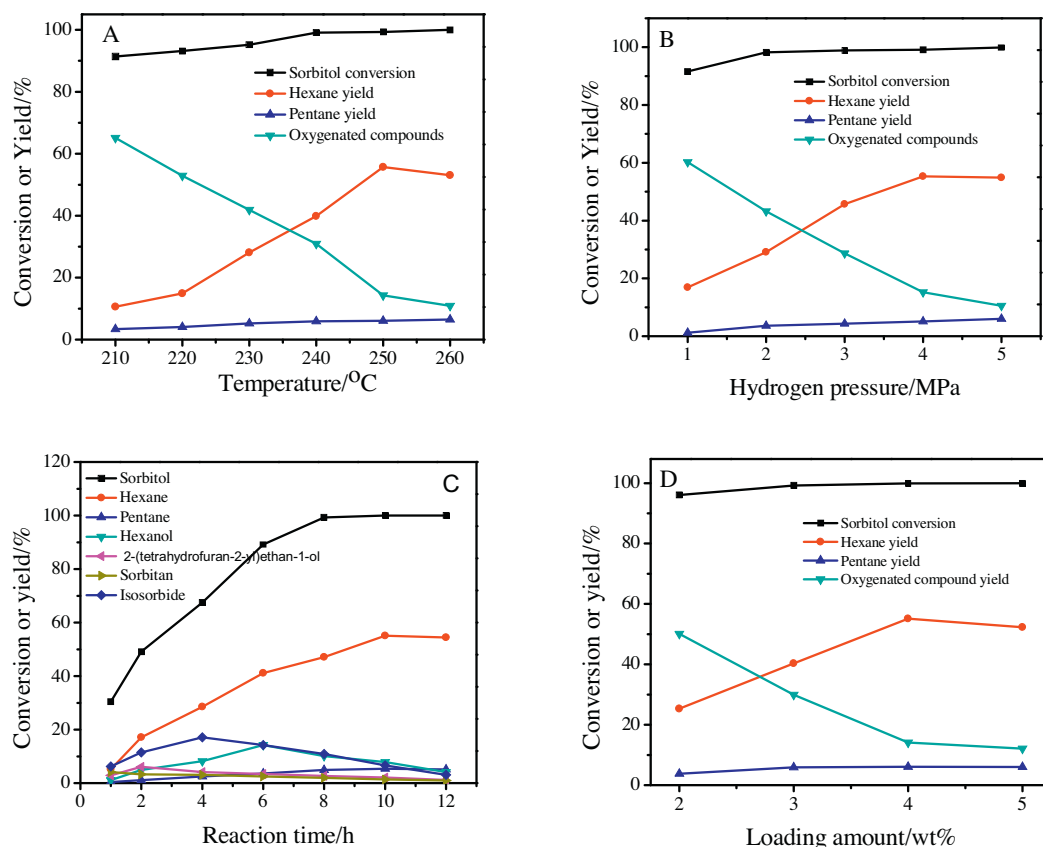
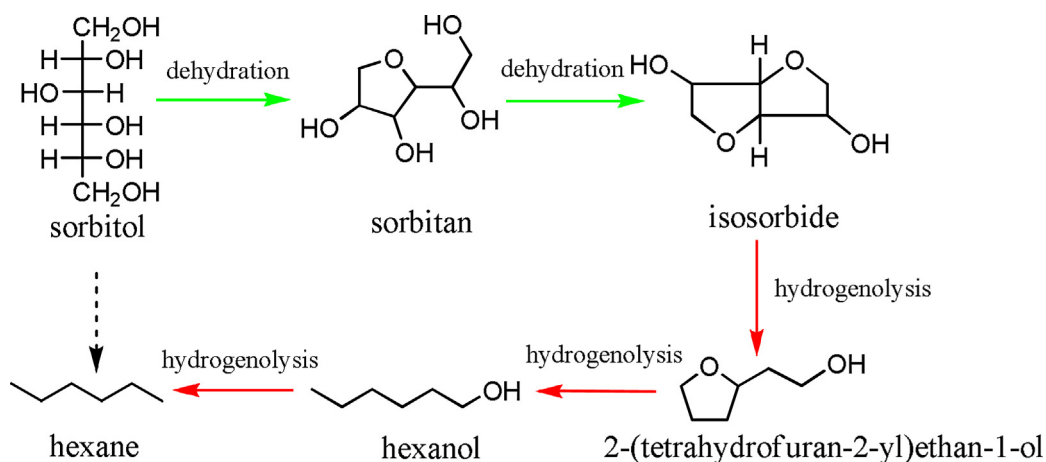


Fig. 2. Influence of reaction conditions on the hydrogenolysis of sorbitol in aqueous medium over Pt/NbOPO₄. (A) Effect of reaction temperature, 4 MPa H₂ initial pressure, 10 h; (B) effect of H₂ initial pressure, 250 °C, 10 h; (C) effect of reaction time, 250 °C, 4 MPa H₂ initial pressure; (D) effect of loading amount, 250 °C, 10 h, 4 MPa. Reaction condition: sorbitol (1 g), H₂O (20 g), catalysts (0.3 g).

parison (Fig. 5). The results of activation energy are summarized in Table 3. We could know combining with corresponding activity data that the high activity for Pt/NbOPO₄ catalyst was related to its relatively low activation energies. The activation energy of Pt/H-Beta catalyst for sorbitol dehydration is higher than that of Pt/NbOPO₄ catalyst, which would be attributed to the strong and high acidity of NbOPO₄; the activation energy for isosorbide hydrogenolysis is also higher than that of Pt/NbOPO₄, which would be attributed to the promotion effect of NbO_x species on C–O bond cleavage and strong acidity of Pt/NbOPO₄. All of these determined that Pt/NbOPO₄ was an excellent catalyst for the hydrodeoxygenation of sorbitol to alkanes in aqueous media.

3.5. The reusability of Pt/NbOPO₄ catalyst

The recyclability of the Pt/NbOPO₄ catalyst in sorbitol hydrogenolysis was then investigated under the selected conditions of 240 °C, 4 MPa H₂ and 6 h in batch reactor. After each reaction cycle, the catalyst was first separated from liquid phase by centrifugation and dried for the next run. Fresh catalyst was not added to compensate any loss of the catalyst in the prior run. Fig. 6 shows that the sorbitol conversion reached 74% (<100%), almost 40% yield of hexane and pentane was obtained. After four successive runs, no significant decline in sorbitol conversion and alkane yields were observed, which indicated that the reusability of catalyst was excel-



Scheme 1. The reaction pathway of sorbitol hydrogenolysis into hexane over Pt/NbOPO₄.

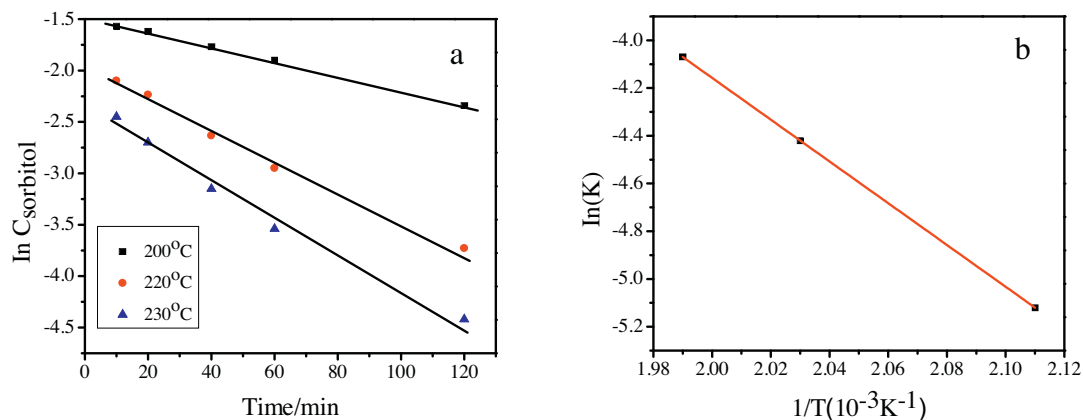


Fig. 3. Determination of the activation energy from Arrhenius equation for sorbitol dehydration. (a) Plots of $\ln(C_{\text{sorbitol}})$ vs. time at different reaction temperatures; (b) Arrhenius plot of $\ln k$ vs. $10^3/T$ for sorbitol dehydration.

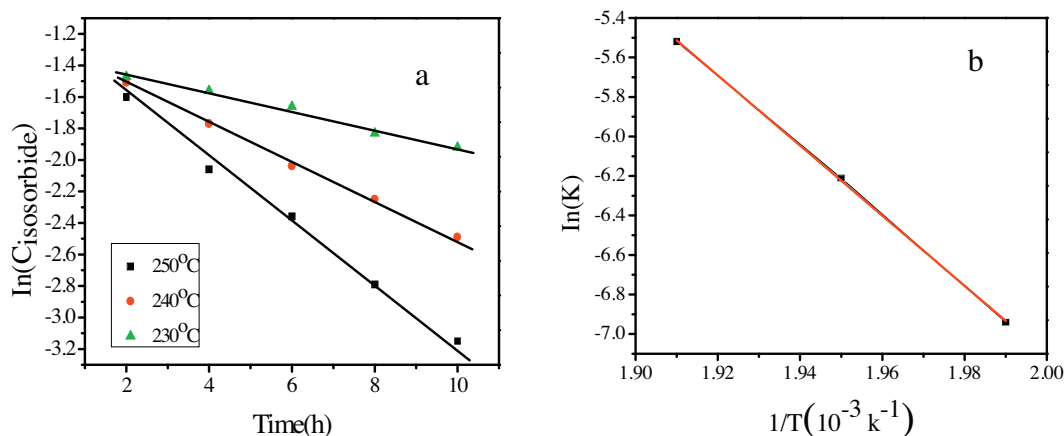


Fig. 4. Determination of the activation energy from Arrhenius equation for isosorbide hydrogenolysis. (a) Plots of $\ln(C_{\text{isosorbide}})$ vs. time at different reaction temperatures; (b) Arrhenius plot of $\ln k$ vs. $10^3/T$ for isosorbide hydrogenolysis.

lent. Inductively coupled plasma spectrometer (ICP) analysis of reaction liquid showed that the leaching of Pt is negligible (the percentage of the initial Pt on the catalyst leached: 0.09%). The slight decrease of alkanes yield may be due to the leaching of P species (1.4%) [36], which may lead to the reduction of acid amount. TEM images (Fig. 7) showed that the growth or aggregation of Pt was not observed for used catalyst compared with fresh one. TG curves demonstrated that there are only 5% carbon deposition on the used Pt/NbOPO₄ catalyst (Fig. 8), which also may be one reason for decreasing of hexane slightly. The above evidence indicated that

the Pt/NbOPO₄ present good stability for sorbitol hydrogenolysis into alkanes in aqueous media.

3.6. Performance on fixed bed reactor

The production of alkanes (C1–C6) from sorbitol was also performed in a fixed-bed reactor to further test the stability of the Pt/NbOPO₄ catalyst using a 10 wt% solution of sorbitol as feed stock. Fig. 9 shows a 100 h time-on-stream life result by operated at 230 °C, 50 bar total pressure, WHSV = 1.2 h^{−1} and 40 ml min^{−1}

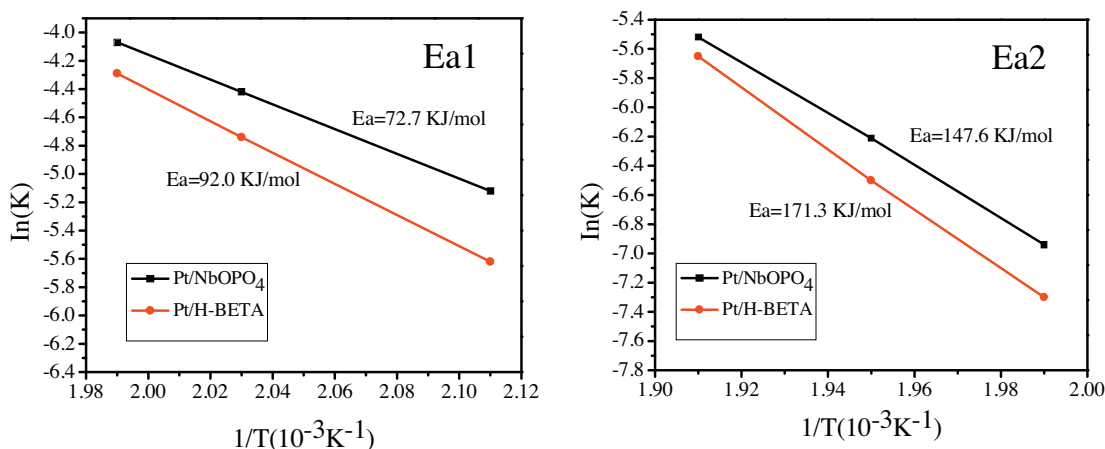


Fig. 5. Arrhenius plot of $\ln k$ vs. $10^3/T$ for sorbitol dehydration (left) and isosorbide hydrogenolysis (right) over Pt-based catalysts.

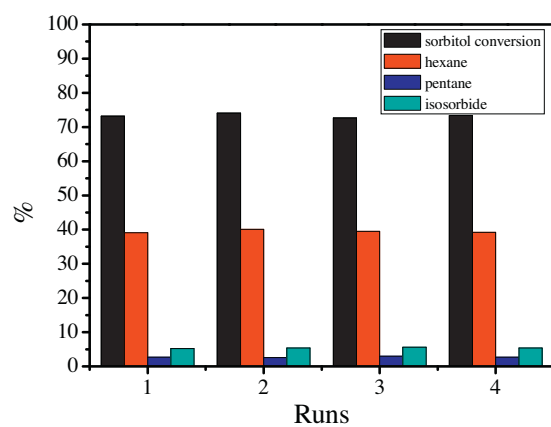


Fig. 6. Reuse of Pt/NbOPO₄ catalyst for the hydrogenolysis of sorbitol into liquid alkanes. Reaction conditions: sorbitol (1 g), H₂O (20 g), catalysts (0.3 g), 240 °C, 4 MPa H₂, 6 h.

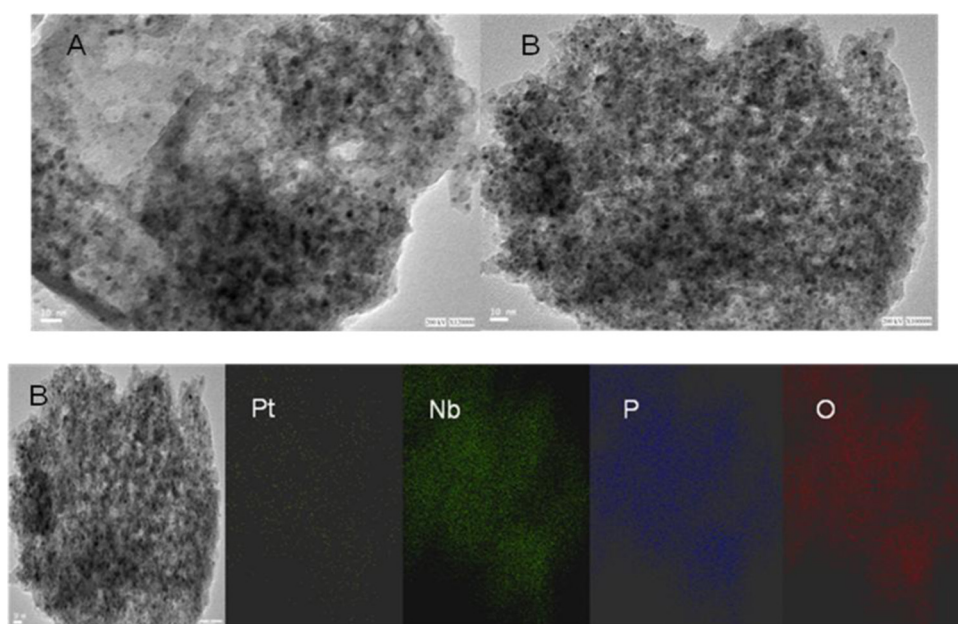


Fig. 7. TEM images and element mapping of 4 wt% Pd/NbOPO₄. (A): used Pd/NbOPO₄ after five runs reaction test; B): fresh Pd/NbOPO₄; the mapping images belong to fresh catalyst.

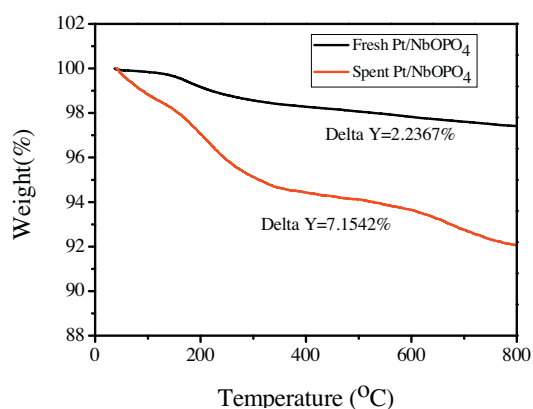


Fig. 8. TG profile of fresh Pt/NbOPO₄ catalyst and spent Pt/NbOPO₄ catalyst.

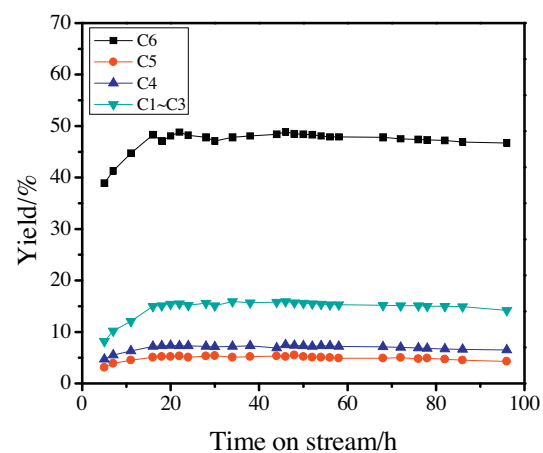


Fig. 9. Production of alkanes (C1~C6) by the direct hydrodeoxygenation of a 10 wt.% sorbitol solution in a fixed-bed reactor over Pt/NbOPO₄ catalyst. Weight hourly space velocity: 1.2 h⁻¹. Reaction conditions: 230 °C, 5 MPa H₂, gas-flow rate: 20 ml/min.

gas-flow rate. Obviously, the catalyst showed an excellent stability with almost no change of sorbitol conversion and product distribution, totally different from those over Pt/ZrP and Pt-ReO_x/C Catalysts [24]. In the later, the Pt/Zr-P catalyst underwent phase transformation from amorphous phase to crystalline rhombohedral framework and led to rearrangement of active sites and the change of products distribution.

4. Conclusion

Multifunctional Pt/NbOPO₄ catalyst was found to have excellent catalytic performance for hexane production from sorbitol in aqueous media. The effects of reaction temperature, hydrogen pressure, reaction time and loading amount of Pt on the catalytic performance were investigated and 60% of C6 and C5 alkanes yield was obtained at optimal condition. The stability of catalyst was investigated by batch reaction and fix-bed reaction, this catalyst was demonstrated to be stable after 100 h only with slight loss in catalytic activity. Therefore, Pt/NbOPO₄ is an effective and stable catalyst for hexane production from sorbitol in aqueous media. The investigation of reaction route indicated that several reactions occur in this process including dehydration, hydrogenolysis reactions and CC bond cleavage. The whole process was divided into two step—dehydration and hydrogenolysis steps. Isosorbide is the final product of dehydration reaction and also an important intermediate in this process. Isosorbide then undergoes ring opening hydrogenation reactions and hydrogenolysis step to form C6 hexane. The activation energy of sorbitol dehydration and isosorbide hydrogenolysis was calculated, that is 72.7 kJ/mol and 147.6 kJ/mol, respectively. The above results showed that isosorbide hydrogenolysis is a rate-determine step.

Acknowledgements

This project was supported financially by the NSFC of China (No. 21273071), the Science and Technology Commission of Shanghai Municipality (13520711400, 13JC1401902, 10dz2220500) and the Fundamental Research Funds for the Central Universities, China.

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